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Report of

17TH CORN AND WHEAT UTILIZATION CONFERENCE

Northern Utilization Research and Development Division

and

Corn Industries Research Foundation
Technical Committee

of the

Corn Refiners Association, Inc.

Peoria, Illinois
October 15-16, 1968

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SUMMARY

In welcoming visitors to the Conference, Dr. Dimler commented on the scope of the program to be presented. The new wing is now complete. While some staff operations are starting to move in, budget cuts and the rollback to July 1, 1966, employment levels sharply limit the rate at which we can make use of this space. Much greater emphasis in our research planning is being placed on dollar benefits vs. budget costs.

Factors which control selective substitution of sugars were studied and found to be (1) relative reactivity of the hydroxyls; (2) inductive effect of vic groups; and (3) steric hindrance. A choice of mild reagents and/or mild reaction conditions may markedly limit substitution. In starch and other polysaccharides, reactions of hydroxyl groups are further limited by lack of accessibility to hydroxyl groups which are buried in the tertiary structure.

Conditions for reactions of starch with sugars were described which yield new derivatives having pendant sugar residues substituted in the range of 0.2 to 0.9. Amino and thiol derivatives were also prepared.

Hot water-soluble films of exceptionally high clarity, gloss, strength and flexibility were prepared from 50- to 70-percent amylose starch by partial acetylation (D.S. 0.25) and jet-cooking.

Continuous conversion of starch to glucose was attained with columns of amyloglucosidase bound to DEAE-cellulose, but pretreatment of the starch with α -amylase was necessary to prevent blocking the column. Bound enzyme activity was only about one-third that of the free enzyme.

An improved amino acid analytical procedure was described which gives better separation with samples high in glutamic acid. A new internal standard, S- β -(4-pyridylethyl)-L-cysteine, has been prepared which has allowed complete use of the internal standard calculation procedure, resulting in faster and more accurate calculations.

A new rapid method for amylose determination was described which is now used in connection with a cooperative breeding program to develop high-amylose corn. It is based on a dimethylsulfoxide-starch soluble complex which can be readily separated from other corn components, yielding a solution suitable for determination of starch polarimetrically and of amylose-iodine blue value with a colorimeter.

Results of a two-year survey for mycotoxins in corn from three locations yielded 35 apparently positive samples by TLC analysis out of 1,311 samples analyzed. Duckling tests were negative for the 5 samples in grades 2, 3, and 4; weakly positive for grade 5; and positive for all 25 samples in sample grade.

The effectiveness of various treatments for reducing microbial populations in corn and dry-milled corn products was studied. While sanitary precautions and treatments at various phases of the milling process are helpful, treatment of final products after separation with heat or propylene oxide seems most reliable and practical.

Gelatinization of corn grits by roll cooking (both steam-heated and gas-fired), extrusion cooking, and steaming was studied and properties of products were compared. Conditions were described by which products having a variety of characteristics may be produced; specifically, it was shown that gelatinized cornmeal having water absorption index, cooked paste viscosity and other properties suitable for use in "CSM" and other food and industrial products could be prepared.

A new and highly effective starch-resorcinol-formaldehyde resin has been developed which appears useful as a reinforcing agent for rubber. Conditions for preparation of SBR masterbatches were described. Tensile strengths up to 2,540 p.s.i. were attained with vulcanizates containing 45 p.h.r. starch and 4.6 percent resorcinol.

Reactions between starch xanthate of 0.11-0.55 D.S. and polyethylenimine (PEI) of 600-100,000 M.W. were studied in aqueous medium. Chemical and physical properties of products were described and possible use as a paper additive was suggested.

Starch xanthate-PEI reaction products were evaluated as wet-end papermaking additives. Unbleached kraft papers containing 5 to 10 percent PEI showed dry-strength improvement comparable to commercial cationic starches, but bleached pulps were not improved.

Since 1960, field shelling of corn has increased from 18 percent to over 64 percent of the corn harvest. The bulk of this corn contains moisture between 20 percent and 30 percent, so that artificial drying is necessary before it can be stored or marketed. The high rate of harvesting and drying has resulted in market corn with quality characteristics different from that of 20 years ago.

The discovery that opaque-2 and floury-2 genetic types of corn have proteins of nutritional quality superior to ordinary corn has made necessary a new evaluation of the use of corn for food and feed. Progress in developing new hybrids with improved nutritional quality was reviewed and preliminary evaluation of field performance and value in practical feeding trials was demonstrated.

Over 50 percent of Illinois corn acreage is now treated with preemergence herbicides and 40 percent receives postemergence treatment. Herbicide toxicity and persistence was reviewed. Although continued vigilance and strict adherence to recommended practices is advisable, currently used herbicides present no apparent problems for corn processors.

Insecticides of the organo chlorine, organo phosphate, and carbamate types were discussed in regard to structure, mode of action, toxicity and persistency. While the organo chlorine (e.g., DDT) insecticides are fat-soluble and subject to serious progressive concentration along a wildlife food chain, levels found in corn products would require consumption of over 188 pounds of grain per day to approach hazardous levels. When ingested, organo phosphate and carbamate types are detoxified and excreted.

In open discussion, a number of areas for needed research were reviewed. These include physical chemical relationships in starch granule swelling, adhesion, rheology of pastes, water management, properties of starch from new genetic types of corn, steeping, new rapid analytical techniques, relation between commercial grade and processing quality to give an indication of the scope of interest.

PROGRAM

Morning Session, October 15

8:30 a.m.	Introductory Comments and Welcoming Remarks	R. J. Dimler
9:00 a.m.	Selective Acylation of Hydroxyl Groups in Sugars and Starches	J. Lehrfeld
9:25 a.m.	New Derivatives and Reactions of Starch and Model Compounds	W. M. Doane
9:45 a.m.	Some Properties of Partially Acetylated High-Amylose Corn Starch and Its Films	A. M. Mark
10:05 a.m.	Intermission	
10:25 a.m.	Immobilized Enzymes	G. W. Strandberg
10:45 a.m.	New Amino Acid Analytical Techniques Applied to Corn and Corn Milled Fractions	J. F. Cavins
11:10 a.m.	A Rapid Method for Amylose Determination in High-Amylose Corns	M. J. Wolf
11:30 a.m.	Mycotoxins in Corn	Alex Ciegler
11:55 a.m.	Group Photograph	
12:15 p.m.	Luncheon	

Afternoon Session, October 15

1:30 p.m.	Reducing Microbial Populations in Corn and Dry-Milled Corn Products	V. F. Pfeifer
1:55 p.m.	Comparative Studies on Gelatinization of Corn Grits by Roll Cooking, Extrusion Cooking and Steaming	R. A. Anderson
2:20 p.m.	Progress in Use of Starch as a Reinforcing Agent in Rubber	R. A. Buchanan
2:45 p.m.	Starch Xanthate-Polyethylenimine (PEI) Reaction	G. G. Maher

3:05 p.m.	Intermission	
3:30 p.m.	Evaluation of Starch Xanthate-PEI Reaction Product in Paper	B. T. Hofreiter
3:50 p.m.	General Discussion	
4:30 p.m.	Adjourn	

Morning Session, October 16

8:30 a.m.	Harvesting, Conditioning, and Storage Techniques for Shelled Corn	G. C. Shove
9:10 a.m.	Recent Developments in Corn Breeding With Respect to Corn Quality	D. E. Alexander
9:50 a.m.	Intermission	
10:10 a.m.	Herbicides for Corn--Use and Consumer Protection	E. L. Knake
10:50 a.m.	Herbicide and Pesticide Residues in Cereal Grains	H. B. Sinclair
11:15 a.m.	Problems and Needs of the Corn Wet Milling Industry (open discussion)	W. G. DeWitt
12:00 noon	Adjourn	

INTRODUCTORY COMMENTS AND WELCOMING REMARKS

R. J. Dimler

I want to welcome you to the Northern Division. Dr. F. R. Senti had hoped to be present, but could not attend, being caught in preparations for a trip to India.

The program for the day covers a reasonable cross-section of this Division's research on corn, including both basic and applied research; analytical and physical chemistry, microbiology, chemical structure and reactions, etc. Studies are directed heavily to starch and carbohydrates, but there is increasing emphasis on proteins, minor components, the corn kernel itself, and corn processing. Summary reports of utilization research for each fiscal year are available.

The new wing is now ours. We own it. When Congress provides a new building, they provide the General Services Administration (GSA) only with funds to construct the building and its associated fixed equipment. We are dependent on later appropriations for staff and laboratory equipment. GSA has turned the building over to us and we are starting to move some people into it. Our present staff numbers around 450 and we expect to eventually add another 150 more, including supporting service staff. Just when we can do this we do not know.

We cannot pinpoint when we will have additional funds, but we are presently putting increased emphasis on cereals in papermaking, soybeans and soy products in foods, and research on soybean meal properties. We hope to capitalize further on our new crops screening program as we have with crambe and kenaf.

The budget situation is clouded. The 10 percent surtax bill included (1) a \$6 billion reduction in federal spending and, (2) a rollback in personnel to July 1, 1966, levels. Last year Congress kept us very close to the previous year's actual expenses in spite of higher costs, and we have had a further 5 percent overall reduction. Until September 1, we have had an absolute freeze on new hiring except for prior commitments; now we can fill only one out of two vacancies. There has, however, been no reduction in force ordered, the reduced worker level being expected to be attained by attrition.

The squeeze is on all over. The personnel reductions cited above will effect some savings, but major decreases will come in money for contracts and grants and for some equipment purchases.

For over a year we have been in the throes of looking at program planning in terms of benefit to USDA and the public--showing tangible benefits from present research and that proposed. We have not been negligent in this before but we need now to get everything that we can in terms of dollar benefits vs. budget costs. Other benefits, such as social, welfare, antipollution, etc., carry some weight, but dollar values must be stated. This hits "basic" research. It will not cut it out, but it will be more difficult to set up and promote new studies. We must cite potential relationships to a tangible goal--the sort of thing you are in business for. We need from this group a feedback on the value to you of this research.

SELECTIVE ACYLATION OF SUGARS AND STARCHES

Jacob Lehrfeld

Partial acylation of sugars gives a wide spectrum of products. Hexoses treated with a deficiency of an acylating reagent, e.g., acetic anhydride, acetyl chloride, benzoyl chloride, acetic acid, give a variety of mono-, di-, tri-, tetra-, and penta-substituted products. If the reaction conditions are vigorous, the spectrum of products has a random distribution. If the reaction conditions are mild, an increase in the relative proportions of some of the products is noted. In some circumstances the selectivity is so marked that only one or two partially acylated products can be isolated.

Three of the factors which control the selective substitution of sugars are:

1. Relative reactivity of the hydroxyls
 - a. Primary hydroxyls acylate faster than secondary hydroxyls
 - b. Equatorial hydroxyls acylate faster than axial hydroxyls
2. Inductive effect of vic groups (e.g., C₂ hydroxyl in sugars)
3. Steric hindrance--hydroxyl groups that are adjacent to other bulky groups have reduced reactivity

In starch and other polysaccharides, an additional factor has to be considered--accessibility. In unactivated starch only a few hydroxyl groups are available for reaction with acylating reagents. The majority are "buried" in the complex tertiary structure and are inaccessible to the reagents.

NEW DERIVATIVES AND REACTIONS OF STARCH AND MODEL COMPOUNDS

W. M. Doane

Mono- and polysaccharides possessing vicinal trans-hydroxyl groups can be readily coupled with starch via ester linkage. Reaction occurs when the saccharide is first converted into the trans-fused cyclic carbonate derivative and then added to starch in the presence of a basic catalyst. A quantitative reaction results upon addition of methyl 4,6-O-benzylidene- α -D-glucopyranoside 2,3-carbonate and methyl 2,6-di-O-methanesulfonyl- α -D-glucopyranoside 3,4-carbonate to starch in the presence of triethylamine. This reaction may be illustrated as shown in Figure 1. Starch products were prepared with degrees of substitution of pendant sugar residues in a range of 0.2 to 0.9. When aqueous solutions of polysaccharides such as a dextrin cyclic carbonate and a dextran cyclic carbonate are added to aqueous suspensions of starch in the presence of catalyst, interpolysaccharide crosslinks are formed and the starch products precipitate.

The trans-carbonate (or thionocarbonate) group serves as a reactive site for amino and thiol as well as hydroxy compounds. Reaction of the carbohydrate trans-carbonates with amines and amino acids affords the carbamate and thio-carbamate adducts in quantitative yields. Similarly, reaction of the carbonate and thionocarbonate with thiols gives monothio- and dithiocarbonates, respectively.

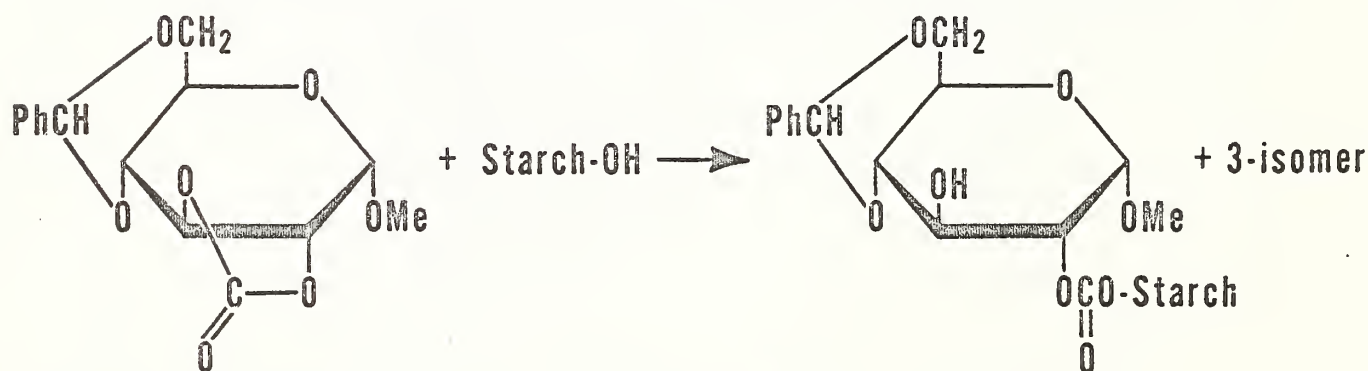


Fig. 1 Reaction of methyl 4,6-O-benzylidene- α -D-glucopyranoside 2,3-carbonate with starch

X
SOME PROPERTIES OF PARTIALLY ACETYLATED HIGH-AMYLOSE
CORN STARCH AND ITS FILMS X

A. M. Mark

Water-soluble film prepared from hydroxypropylated high-amylose corn starch of 70 percent amylose content is commercially available but has poor clarity and flexibility. By partially acetylating (D.S. 0.25) high-amylose corn starch of 50 percent and 70 percent amylose content by a practical procedure and then jet cooking the products, we were able to prepare clear aqueous dispersions which gave hot-water-soluble films of exceptionally high clarity, gloss, strength, and flexibility. The hot water solubility, low oxygen transmission, and potential edibility of the films suggest their utilization in the packaging of dry foods to be subsequently added to hot aqueous fluids. Other possible applications for the products are their use in the preparation of coatings for foods and sizings for paper and textiles.

This paper describes the acetylation procedure and the various methods investigated for disintegrating the granules of the starch acetates to obtain improved aqueous dispersions and thereby films of higher quality than have been available heretofore.

X IMMOBILIZED ENZYMES X

Gerald W. Strandberg

Amyloglucosidase, bound to DEAE-cellulose in 0.05M sodium acetate, pH 4.0, was active in the conversion of starch to glucose. The DEAE-cellulose-bound enzyme was only one-third as active as the free enzyme. Binding of the enzyme resulted in a narrowing of the pH optimum to approximately 4.0 and lowered the temperature optimum to 40°-50° C. as compared to a 60° C. temperature optimum for the free enzyme. Concentrations of acetate buffer above 0.1M disrupted the DEAE-cellulose-enzyme complex. Columns were used with some success for the continuous conversion of starch. Pretreatment of the starch with α -amylase and clarification was necessary to prevent blocking of the column.

X
NEW AMINO ACID ANALYTICAL TECHNIQUES APPLIED TO
CORN AND CORN MILLED FRACTIONSX

J. F. Cavins

Amino acid analysis of ingredients is important in producing nutritious mixed feeds. Considerable variability in analytical results can be found. Differences in samples can account for some variation; however, analytical differences are sometimes at fault. In an effort to overcome analytical variability we have compared various methods to find the most reliable ones and in some cases we have endeavored to find new methods. Sample type to a great extent dictates the method of analysis used. Many hydrolysis procedures have been presented and the system chosen depends on the sample type. We have changed our chromatography procedure to obtain better separation on samples containing large amounts of glutamic acid in the hydrolysate. A new internal standard, S- β -(4-pyridylethyl)-L-cysteine (PEC) has been prepared in our laboratory for use on the short column which has allowed complete use of the internal standard calculation procedure. The cystine residues in a protein can be reduced with mercaptoethanol and alkylated with 4-vinylpyridine to produce PEC in the hydrolysate. This reaction has been shown to be a reliable method for cystine analysis. Reaction of vinyl compounds with functional groups in proteins can also be applied to the lysine residues. We have modified the epsilon-amino groups of lysine with acrylonitrile and are developing this into a method for available lysine.

A RAPID METHOD FOR AMYLOSE DETERMINATION IN HIGH-AMYLOSE CORNS

M. J. Wolf

A relatively rapid method was developed for the determination of amylose in maize starch. Approximately 1-gram samples of corn (4 or 5 kernels) are ground in 90 percent dimethyl sulfoxide (DMSO) in a vibratory mill for 3 minutes. This treatment breaks open starch-containing cells and swells or dissolves starch granules. Solution of starch granules is completed by continuous shaking of the DMSO extract at room temperature for 24 hours. The insoluble residue is settled by gravity (or centrifuged) and discarded. A 10-ml. aliquot of the clear supernatant solution is shaken with 3 volumes of absolute ethanol to precipitate a DMSO-starch complex. Lipids, zein, and sugars remain in solution and are discarded. The DMSO-starch is recovered by centrifuging and redissolved in 90 percent DMSO. The blue value is determined on a 0.5 or 1.0 ml. aliquot of this solution; absorbance is measured at 605 m μ with a Beckman B colorimeter.

Starch is determined polarimetrically on a separate aliquot of the same solution in a Bendix automatic polarimeter. The value for specific rotation of starch dissolved in 90 percent DMSO and measured in green light ($[\alpha]_D^{20}$ 546 m μ) is 220°. The same value for specific rotation applies to whole starches, purified amyloses, and amylopectins. Precision of the method is about ± 1.5 percent (Standard Deviation). Ordinary corn starches are much harder to dissolve in DMSO than amylomaize starches or waxy starches. Despite its high oil content, the germ does not interfere with amylose determination. However, free oil is entrapped in fibrous residues of ground corn and interferes with settling. Pericarp tissues contribute no detectable optical rotation to extracts of corn.

The new procedure is employed at NU in the determination of amylose in maize selections in connection with a cooperative corn breeding program to develop commercial high-amylose corn.

MYCOTOXINS IN CORN

Alex Ciegler

Corn from commercial markets was surveyed for the presence of aflatoxin. A total of 1,311 samples were collected in three locations (Peoria, Des Moines, Omaha) from two crop years, 1965 and 1966. Samples were extracted by the "Celite column" method developed by FDA for peanuts and peanut products. Thirty-five samples appeared to be positive by thin-layer chromatography (25 in sample grade, a 7.1 percent incidence; and 5 in grade 5, a 1.8 percent incidence). The remaining positives were evenly distributed in the four other grades. The incidence was about the same in the three locations sampled. Aflatoxin occurred in 3.2 percent of the samples collected in 1965 and in 1.9 percent of those collected in 1966. The duckling test was negative for the apparent positives by TLC in grades 2, 3, and 4. The duckling response was weak for samples from grade 5. TLC-positives from sample grade all gave positive duckling tests.

REDUCING MICROBIAL POPULATIONS IN CORN AND DRY-MILLED CORN PRODUCTS

V. F. Pfeifer

The problem of microorganisms in starches, cereals, and cereal fractions is especially important to manufacturers of refrigerated, frozen, and cooked convenience foods, baby foods, and canned foods. A total microbial count below 5,000 per gram has been required in many of the dry ingredients used in convenience foods, and additional requirements are placed on the numbers of thermophilic spores that can be permitted. For total thermophilic spores, the maximum permitted by the National Canners Association standards for starch and sugar to be used in canned foods is 150 spores for any 10-gram sample, or an average of not over 125 spores for 5 samples. For flat-sour spores, which attack carbohydrates to form acid but no gas, the maximum is 75 spores for any one 10-gram sample, or an average of not over 50 spores in 5 samples.

Reduction in microbial counts of the dry-milled products from corn can be accomplished as follows:

1. Treat the corn to be milled to reduce its load of microorganisms.
2. Apply efficient dry-cleaning methods to remove part of the bacteria and molds.
3. Apply sanitizing agents to the wash water and to the temper waters.
4. Carry out the drying step in a manner to accentuate the reduction of microorganisms always obtained in this step.
5. Combine the various streams produced in milling in a manner to exclude much of the bacteria and molds.
6. Treat the separated products individually.

Of course, any treatments made of the corn or degerminated products will be effective only if contamination is prevented in subsequent milling. Some studies have been carried out at NU in each of these areas, using a laboratory dry-milling procedure that gave results somewhat comparable to those obtained with commercial equipment.

Even though corn was stored at 40° F. or below, it was found that microorganisms died off quite rapidly during storage, and the dry-milled products prepared from the corn improved markedly over a 7-month corn storage period. Highest microbial populations were always highest in the flour and feed fractions, lowest in the grits fractions, and intermediate in meal fractions. Degerminator fines were highest in molds and also quite high in bacteria.

Treatments of the corn that were especially effective in reducing microbial counts in the dry-milled products were: immersion of the corn in hot sanitizing solutions (0.1 percent solution) at 180° F. for 1 minute before milling; steaming of corn at atmospheric pressure for 30 to 60 seconds before milling;

pretempering corn to 16 percent moisture or higher, and heating at temperatures of 180° to 212° F. for times up to 60 minutes before milling. Heating the degerminator streams before milling was also effective in yielding dry-milled products with reduced microbial counts. These methods appear to be relatively simple and practical but require careful milling to prevent subsequent pickup of microorganisms.

Microbial counts in dry-milled corn products are reduced by heating at 12 to 14 percent moisture content. Typical conditions for reduction to below 5,000 per gram included treatment for 3 days at 135° F., 2 days at 145° F., 1 hour at 180° F., or 10 minutes at 212° F. Rates of destruction for bacteria and molds were rather similar, and were comparable to those previously found for wheat and wheat flour. Amylograph curves showed that heat treatments increased thickening properties of the dry-milled products in addition to destroying microorganisms.

Treatments of corn flour with ultraviolet light in efforts to reduce microbial counts were unsuccessful.

Thermophilic spores and bacteria in dry-milled corn products can be reduced somewhat by washing the corn in hot sanitizing solutions before milling, or by heating the dry-milled product itself after it has been separated. Almost complete elimination of thermophiles can be effected by treating the dry-milled products with propylene oxide under suitable conditions of time, temperature, and epoxide concentration. Resulting products would meet all requirements of the National Canners Association. Amylograph curves of products from these experiments showed that the products were improved in thickening properties also.

The information developed in the NU studies can be summarized as follows:

1. The highest microbial populations are found in the flour and feed fractions, with degerminator fines usually highest, at least in molds. Lowest counts are in the grits fraction.
2. Reduction in microbial populations can be accomplished by treating the corn before processing, by treating degerminator streams before proceeding with the milling, or by treating the products after they have been separated.
3. When the corn or degerminator streams are treated, precautions must be exercised to prevent contamination during subsequent milling.
4. Heat treatments appear to be the most practical methods at present, when used in combination with efficient grain cleaning and good milling techniques.
5. Reduction of thermophiles entails efficient cleaning and water washing of corn before milling, in order to eliminate soil particles, preferably with water-containing chlorine or sanitizing agents.
6. Some reduction of thermophiles can be obtained by heat treatments, but treatment of dry-milled fractions with propylene oxide is very effective and could be relied on to produce materials meeting standards of the National Canners Association.
7. Treatment of the final products after separation by milling appears the most practical method for reducing microbial populations with the least interference to established milling procedures.

COMPARATIVE STUDIES ON GELATINIZATION OF CORN GRITS
BY ROLL COOKING, EXTRUSION COOKING, AND STEAMING

R. A. Anderson

To most of you, the gelatinization of corn starch is an old story, for gelatinized corn starch and corn flour have been marketed by your industry and the corn dry millers for more than 50 years for various industrial and food applications. The more economical materials now available commercially are prepared by passing corn grits, meal, or flour between gas- or steam-heated steel rolls, where the degree of gelatinization depends upon the moisture content, particle size, temperature, roll pressure, rate of throughput, or duration of heating and precooking. Products vary in water absorption and solubility and in viscosity of the cooked and uncooked suspensions in water, so that numerous requirements for different applications can be met. The use of extruders for the gelatinization of cereal products has become popular within recent years, and such equipment is now used extensively in making snacks and breakfast cereals, as well as for industrial products of various kinds.

Recent programs for world-wide feeding involve the production of a food blend known as "Blended Food Product, Formula No. 2" and more commonly called CSM, which contains partially gelatinized corn meal in admixture with soy flour, nonfat dry milk, vitamins, and minerals. CSM cooked with 9 to 10 parts of water for 2 minutes yields a gruel having a consistency suitable for supplemental feeding infants and young children. Corn meal processed for this product can be either roll- or extrusion-cooked. Even though roll- and extrusion-cooking are carried out commercially, little information has been published about the relationship between operating conditions and product characteristics.

We have studied the processing of corn grits by roll- and extrusion-cooking over a range of operating conditions, including those for producing corn meal suitable for use in CSM. We have also carried out studies on the use of live steam as a means of gelatinization. This report will bring together the work of three members of the Engineering Laboratory, and I acknowledge the work of Howard Conway who conducted the extrusion-cooking studies, and Al Peplinski who did the work on the use of live steam for cooking corn grits.

In all the studies, commercial corn grits were used, and analyses are given in Table 1.

Table 1. Analyses of Corn and Sorghum Grits Used in Tests

	Chemical Analysis ^{1/}				Screen Analysis ^{1/}			
	Moisture, %	Protein, %	Ash, %	Fat %	+14	+20	+30	-30
Corn Grits	14.0	8.1	0.37	0.5	1	87	12	41
Sorghum Grits	12.0	9.2	0.41	0.8	4	84	11	1

^{1/} As is basis.

Roll-cooking was carried out on a laboratory Buflovak double drum dryer, shown in Figure 1. The dryer has two chrome-plated rolls, each 6 inches in diameter and 7-5/8 inches long, with a total area of 2 square feet. The rolls were heated by steam, under pressures up to 100 p.s.i.g. Grits were fed to the rolls by a vibratory feeder. Roll temperatures up to 300° F. were obtained with this equipment. For higher temperatures a pilot plant gas-fired roll dryer was used. The equipment shown in Figure 2 is fitted with two chrome-plated steel rolls, 12 inches in diameter and 18 inches long. Temperatures up to 700° F. are obtainable with this dryer.

Extrusion was carried out in a Killion K-100 Standard plastics extruder having a 1 inch diameter barrel and a 20 inch effective screw length (Figure 3). The screws with this extruder have an increasing root diameter over the last 10 inches of length to compress the feed. Two screws were used with compression ratios of 3:1 and 1.5:1. Temperature of the extruder barrel was regulated by electrical heaters controlled thermostatically to give temperatures up to 600° F. A separate thermostat and heater combination was applied to each half of the barrel.

The equipment used to steam the grits was a sterilizing autoclave in which live steam is admitted to make direct contact with grits.

Gelatinized materials were evaluated by water absorption, water solubility, and amylograph viscosity patterns.

The water-absorption index equalled the weight of gel obtained per gram of dry sample in a modification of the method described by Kite, Schoch, and Leach for measuring swelling power of starch. A 2.5-gram sample of ground product (-60 mesh) was suspended in 30 ml. of water at 30° C. in a 50-ml. centrifuge tube, stirred intermittently over a 30-minute period, and centrifuged at 3,000 X G for 10 minutes. The supernatant liquor was poured carefully into a tared evaporating dish. The remaining gel was weighed and the water-absorption index calculated from its weight.

As an index of water solubility, the amount of dried solids recovered by evaporating the supernatant from the water absorption test just described was expressed as percentage of dry solids in the 2.5 gram sample.

The amylograph test was carried out with 500 grams of 9 percent (dry basis) suspension of the sample (-60 mesh), heating it from 29° to 50° C. in 44 minutes, holding at 95° C. for 16 minutes, and then cooling to 50° C. in 30 minutes. The amylograph test indicates the suitability of a corn meal for use in CSM, with the final cooked paste viscosity (50° C.) as the criterion of suitability. CSM for purchase by USDA must form an 11 percent cooked gruel of specified consistency as measured with a Bostwick consistometer. Corn meal that will yield a CSM having a cooked consistency meeting this specification has a final cooked paste viscosity (50° C.) by this amylograph test in the range of about 200 to 700 Brabender units (B.U.).

In the following discussion, I will compare roll- and extrusion-cooking as they are applied to making a variety of gelatinized corn products over a wide range of conditions, and then compare the three methods as they are used to make a partially gelatinized product suitable for use in CSM.

In the roll-cooking studies the following variables were investigated: Moisture content of grits over the range 15-30 percent and roll surface temperatures during operation of the steam heated dryer of approximately 255°, 285°, and 300° F., and roll temperatures ranging from 300° to about 570° F. on the gas-fired rolls. Rolls were set cold with a clearance of 0.001 inch and the roll speed was 3 r.p.m.

In the extrusion-cooking studies, the following variables were investigated: Moisture content of grits over the range 10-35 percent, barrel temperatures between 220°-450° F., compression ratio of screw 1.5:1 and 3:1, and extrusion with or without a discharge die.

Moisture content of the grits to be treated was adjusted to the desired value by spraying water on them while mixing and then holding the tempered grits for at least 1 hour.

In Figure 4, we show the effect of temperature and moisture on the water absorption index of roll- and extrusion-cooked corn grits. Two moisture levels were selected, about 15 and 25 percent. Little gelatinization in the roll-cooked products took place at the 15 percent moisture level until about 300° F. temperature was reached, then there was a gradual increase in the water absorption index to about 7 at 500° F., where the water-absorption index began to decrease. At 25 percent moisture, the water-absorption index of the roll-cooked product rose rapidly to a peak of about 8 at 450°-460° F. and then decreased. Excessive heat adversely affects the water-absorption index and quality of product is lessened. Depending on moisture content, some toasting occurs at 465° F. and higher. In contrast, an extrusion-cooked product cooked at 14 percent, has about the same water-absorption index at 260° F. as the 25 percent roll-cooked material cooked at 260° F. The water-absorption index increases rapidly with increasing temperature reaching a maximum of about 7 at 340° F. where the water-absorption index decreases sharply with increasing temperature. The same maximum water-absorption index was reached at 14 percent and 350° F. with extrusion as was reached at 15 percent moisture and 500° F. with roll cooking. This is due to a combination of longer heating time in the extruder with the heated material reaching or exceeding the barrel temperature because of the friction involved and to mechanical shear in the extruder which increases starch degradation. Similar water-absorption index results were obtained at 25 percent moisture, except at a slightly higher level. Maximum water-absorption index was reached at about 350° F. with extrusion-cooking at 25 percent moisture as contrasted to about 450° F. with the roll-cooked product at 25 percent moisture.

Figure 5 gives a comparison of the water solubility indices of products cooked at about the same two moistures over a range of temperature. With roll cooking, water solubility index increases rather slowly with increasing temperature. Somewhere around 550° F., there is an indication of a sharp increase in water solubility index. Other tests have shown that the water solubility index increases almost vertically at this high temperature, reaching a water solubility index of as high as 40 (30 percent, 565° F.; 20 percent, 570° F.). The water solubility index of the extruder-cooked products increased at a greater rate over its entire temperature range reaching 40 and higher some 100° F. sooner than the roll-cooked product. It is interesting to note that the water solubility index of the lower moisture product was higher than for the 25 percent product. This again is probably the result of starch degradation due to shear taking place in extruder.

In Figure 6, I have plotted the amylograph curves for the 25 percent moisture roll- and extrusion-cooked products at maximum water absorption index. Uncooked cold paste viscosities of the two products were about the same. Here the similarity ends. With the roll-cooked products, there is a definite cooking cycle reaching a maximum viscosity of about 500 B.U. The curve then goes through its usual viscosity decrease, then rising on cooling to a final cooked paste viscosity of about 350 B.U. The extrusion-cooked product exhibited a viscosity pattern of no cooking period, gradual decrease in viscosity until the cooling cycle, where there was a slight increase in viscosity to about 150 B.U. In general, with roll cooking (Figure 7), there was an increase in uncooked cold paste viscosities with increasing temperatures up to

550°-570° F., where decomposition of product apparently takes place. Final cooked paste viscosities decrease with increasing processing temperatures. For extrusion cooking at 25 percent moisture (Figure 8), uncooked cold paste viscosity increased to a maximum for the 350° F. sample and then decreased with further temperature increase. Final cooked paste viscosity decreased progressively with temperature, same as roll cooking. Just a word on the effect of shear on the viscosity of the pastes from extruder-cooked grits.

The effect of reducing shear by using a screw with lower compression ratio (1.5:1 instead of 3:1) is shown in Figure 9. Cooking was done at 225° F. and 25 percent moisture. Less shear was produced when the 1.5:1 screw was used, resulting in higher final cooked paste viscosity (50° C.) of 540 B.U.; this is compared with 395 B.U. when the 3:1 screw was used.

The effect of using a discharge die was to introduce additional shear. As shown in Figure 10, cooking here was done at 400° F. and 25 percent moisture. Uncooked cold paste viscosity (29° C.) was reduced from 250 B.U. when no discharge die was used to 110 B.U. when the outlet was restricted by a 1/4 inch discharge die. Final cooked paste viscosity (50° C.) was reduced from 100 B.U. to 70 B.U.

The use of live steam to cook corn grits is another approach to the study of gelatinization of cereal products. Here the grits were tempered for about 16 hours to 15-25 percent moisture and held in the autoclave for 5-45 minutes at temperatures ranging from 212° to 250° F. After treatment the grits were air-dried to about 11 percent moisture. Table 2 shows the

Table 2. Water-Absorption Index of Steamed Corn Grits

Temper Moisture %	Time min.	Water Absorption Index at		
		212° F.	230° F.	250° F.
15 ↓	15	2.6	3.0	3.6
	30	2.9	3.3	3.8
	45	3.0	3.3	4.1
20 ↓	15	2.8	3.5	4.4
	30	2.9	3.6	4.4
	45	3.0	3.6	4.5
25 ↓	15	3.0	3.7	4.6
	30	3.3	3.8	4.7
	45	3.4	4.3	4.4

differences in water-absorption index when the corn grits were exposed to steam under a variety of conditions. In general, there was an increase in the water-absorption index as each of the variables, temperature, moisture, and time were increased. Maximum water absorption indices of 8 were not attained. At the higher temperatures and moistures, water-absorption index values were in the range of products obtained by roll drying which were found suitable for use in CSM (4-5.5).

In Figure 11, we present data comparing the water absorption index of steamed grits with final grit moisture in the autoclave. When 212° and 230° F. temperatures are used, the rate of increase of the water-absorption index with temperature is about the same. At 250° F., a slightly higher rate occurs. It was noted that during steaming from 4 to 80 percent of moisture was picked up by the grits.

Also it was noted that high moisture and temperature for extended times caused a reduction in the final cooked paste viscosity even though the water-absorption index was progressively increasing.

To compare the three cooking methods, I have selected a test for each where the water-absorption index of the cooked product is about the same, falling in the range of 4-5.5. Partially cooked corn grits with this water-absorption index should be satisfactory for inclusion in CSM. This comparison is shown in Table 3. Water-absorption indices given in the first column, of course, are

Table 3. Comparison of Three Methods of Cooking Corn Grits

Processing Methods and Conditions	Water- Absorption Index	Water Solubility Index	Amylograph Final Cooked Paste Viscosity (50° C.) B.U.
Roll cooked:			
22% Moisture, 285° F.	4.7	2.0	720
Extrusion-cooked:			
25% Moisture, 230° F., 3/1 Screw	4.6	6.5	365
Steam-cooked:			
20% Moisture, 250° F., 5 Minutes	4.6	1.2	110

the same, but the water solubility index varied according to the cooking method used. Also, there was a considerable variation in the final cooked paste viscosity of the cooked products. The roll-cooked product has the highest, 720 B.U., with the extrusion-cooked product about half of that, at 365 B.U. Oddly enough, the product obtained by steaming, actually the mildest treatment used, had the lowest paste viscosity, 110 B.U. From this standpoint, the steamed product would not be satisfactory for incorporation into CSM, for it has been established that to meet consistency specifications for CSM, the final cooked paste viscosity should be in excess of about 200 B.U.

To summarize, a large variety of cooked corn products can be prepared by any of the three cooking methods discussed. Slight changes in operating conditions of the cooking equipment can bring about significant changes in absorption, solubility, and viscosity properties of the cooked products. Production of processed materials with higher water absorption and retaining high cooked paste viscosity appears more difficult by direct steaming than by use of the other methods.

Roll-cooking should be better than extrusion-cooking for preparing materials of maximum water absorption and minimum water solubility. Such materials are well suited either for thick gruels or for industrial thickening or gelling agents. Extrusion-cooking should be better for preparing materials of minimum water absorption and maximum water solubility. Such materials are well suited either for beverages or for industrial uses where adhesive properties are desired. Steam-cooking should be suitable for preconditioning before roll- or extrusion-cooking, but it appears that heating time must be held to a minimum.



Fig. 1 Laboratory Buflovak double drum dryer

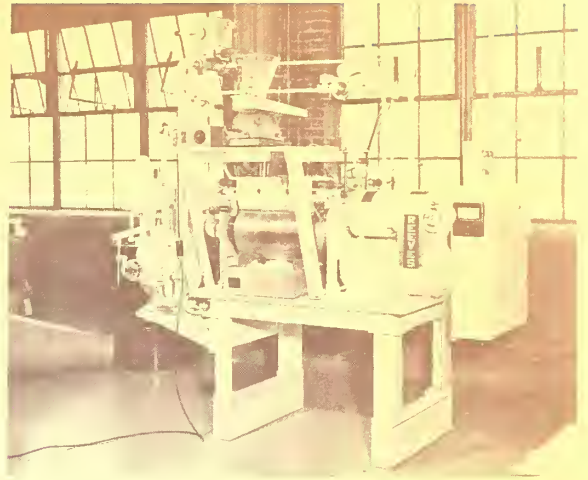


Fig. 2 Pilot plant gas-fired roll dryer



Fig. 3 Killion K-100 standard plastics extruder

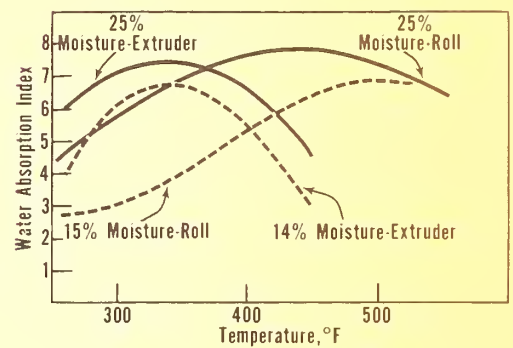


Fig. 4 Comparison of water absorption indices from roll- and extrusion-cooked corn grits

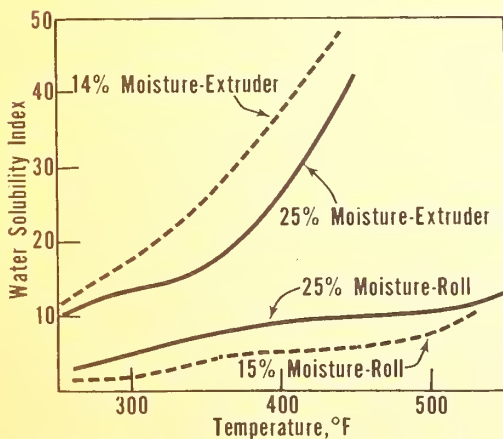


Fig. 5 Comparison of water solubility indices from roll- and extrusion-cooked corn grits

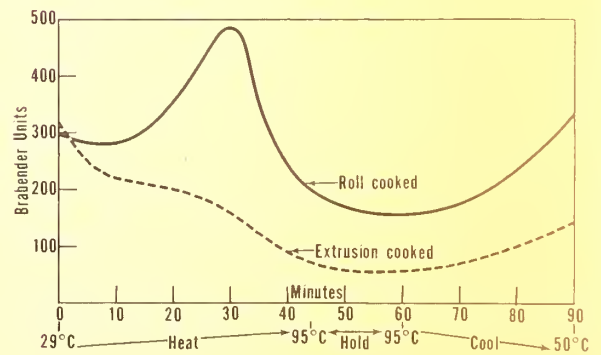


Fig. 6 Amylograph curves for roll- and extrusion-cooked products at maximum water absorption index (25% moisture)

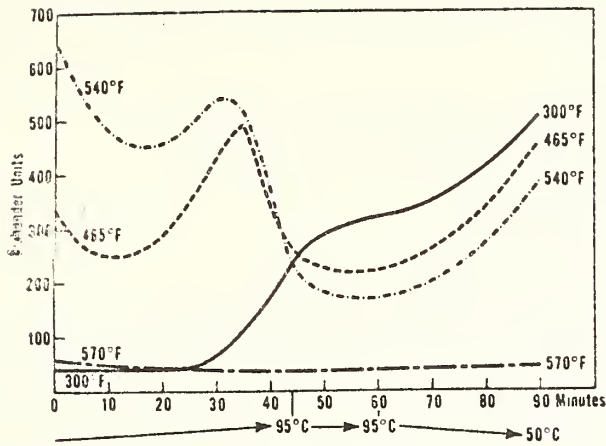


Fig. 7 Cooking corn grits on gas-fired rolls. Effect of temperature on viscosity (20% moisture)

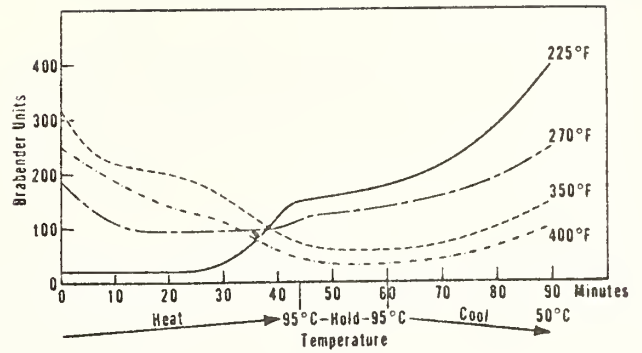


Fig. 8 Temperature effects on viscosity of pastes from extruder-cooked corn grits (3/1 screw ratio, no discharge die)

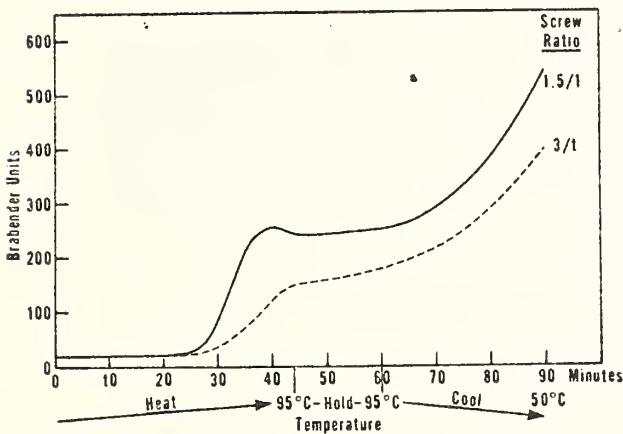


Fig. 9 Shear effects on viscosity of pastes from extruder-cooked corn grits (225°F, No discharge die)

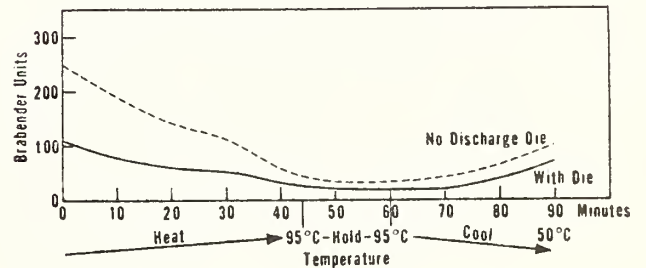


Fig. 10 Effect of additional shear induced by discharge die on viscosity of pastes from extruder-cooked corn grits (400°F, 3/1 screw ratio)

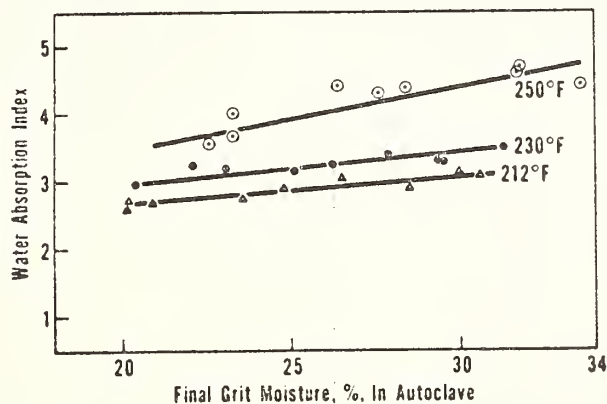


Fig. 11 Water absorption index of steamed grits vs final grits moisture in autoclave

X PROGRESS IN USE OF STARCH AS A REINFORCING AGENT IN RUBBER X

R. A. Buchanan

A new and highly effective starch-based reinforcing agent for rubber has been developed recently. This new product, starch-resorcinol-formaldehyde resin, has somewhat different properties than those of zinc starch xanthate reported at the previous meeting and, thus, enhances opportunities for starch products to capture a significant share of the current 5 billion pounds per year domestic market for reinforcing agents. The starch resin is prepared and incorporated in rubber by adding starch paste, resorcinol, and formaldehyde to latex, stirring the mixture for 30 minutes, then coprecipitating the starch resin and elastomer by addition of ferric sulfate. In all formulations resorcinol and formaldehyde in a 1 to 3 mole ratio, were reacted with gelatinized starch in mixture with elastomer latex. Subsequent addition of ferric sulfate quantitatively coprecipitated starch resin with latex solids. The coprecipitate was dewatered by either filtration or centrifugation and then oven dried. Milling of dried coprecipitate gave a fine particle dispersion of starch in rubber. The starch resin reinforced tensile properties in a variety of elastomers. SBR masterbatches were prepared containing up to 90 parts starch per hundred parts rubber (phr) and from 1.7 to 24.4 percent resorcinol based on starch content. Tensile strength of SBR vulcanizates was greatest (2540 psi) with 45 phr starch and 4.6 percent resorcinol. Tensile strength of SBR with 50 phr starch and 6.0 percent resorcinol was 2,200 psi, about the same as with 50 phr of SRF black.

The starch resin-reinforced rubbers in contrast to rubbers reinforced with zinc starch xanthate are dark colored but stronger, thus the starch resin will be useful where strength but not whiteness or bright coloration is the major consideration. However, further study is needed to determine other important properties of the starch resin-reinforced rubbers such as abrasion resistance; stability to heat, light, ozone, moisture, and chemical agents; and strength properties under extreme temperature conditions.

STARCH XANTHATE-POLYETHYLENIMINE (PEI) REACTION

G. G. Maher

Reactions between starch xanthate of 0.11-0.55 degree of substitution (D.S.) and polyethylenimines of 600-100,000 molecular weight have been studied in aqueous medium. Generally, the reaction mixtures get viscous and become rigid gels. Viscosity development depends primarily on the starch xanthate D.S., the molecular weight of the polyethylenimine, and the molar ratio of polyethylenimine to xanthate groups--increasing as the magnitude in each of these parameters increases. The reaction products can be precipitated by drowning in water and then lowering the pH or by drowning in ethanol. Elemental analyses and spectral absorptions of the precipitated products indicate a thiourethane structure containing 1.75 to 2.5 ethylenimine units per original xanthate group, which would equal a crosslinking bridge having an average length of 3.5 to 5.0 ethylenimine units. In the water-pH drop method precipitation is complete for products from 60,000-100,000 molecular weight polyethylenimine used in the stoichiometric amount (based on the product structure) in the reaction, but for 3,000 molecular weight polyethylenimine about twice the stoichiometric amount is needed, especially with the lowest D.S. xanthate. As the molecular weight of the polyethylenimine is lowered further, there is a tailing off in precipitation, and finally with tetraethylenepentamine there is no precipitation. The best of these aqueous precipitation phenomena were also found to occur in cellulose pulp suspensions, enabling the subsequent formation of a paper product with greatly enhanced strength properties.

EVALUATION OF STARCH XANTHATE-PEI⁵² REACTION PRODUCT IN PAPER

B. T. Hofreiter

Starch xanthate and polyethylenimine reaction products (X-PEI) have been evaluated as wet-end additives in papermaking. Variables studied in the X-PEI reaction and in paper pulp systems include ratio of starch xanthate to PEI reaction time, xanthate D.S., fluidity of original starch, molecular weight of PEI, papermaking pH, level of addition to pulp, and pulp type. It is tentatively concluded that X-PEI compositions containing 5-10 percent PEI give optimum performance. Dry strength of unbleached kraft paper is improved to a degree comparable to or better than is obtained with commercial cationic starches. The additives are well retained, do not adversely affect pulp drainage, and impart a fair degree of wet strength. The additives are ineffective in bleached paper.

HARVESTING, CONDITIONING, AND STORAGE TECHNIQUES FOR SHELLED CORN

Gene C. Shove

Corn harvesting, conditioning, and storage technology has undergone dramatic changes in recent years making it difficult for many corn producers to adapt old and purchase new equipment as rapidly as they would like for the most economical operation of their corn production enterprise. However, they are making changes. For example, in Illinois, field shelling of corn increased from about 18 percent in 1960 to slightly over 64 percent in 1967 with the grain combine equipped with a corn head used for the major portion of the harvest. Recommendations for combining corn are to allow the corn moisture to drop to at least 27 to 28 percent; however, the farmer's desire for an early harvest may cause him to begin harvest at 30 percent or slightly above. The farmer wants an early harvest to allow for fall plowing and to eliminate as much as possible the hazard of bad weather increasing his field losses. In a normal year about 21 days are available for harvesting corn. In a good harvest season, such as 1964, 75 percent of the Illinois corn crop was out of the field by October 30. Even during unfavorable years a high percentage is likely to be harvested by the end of November, such as 88 percent in 1966 and 63 percent in 1967. Almost ideal weather conditions during the fall of 1968 resulted in virtual completion of corn harvest by Thanksgiving.

A large portion of the field shelled corn contains a moisture content in excess of 20 percent creating a need for artificially drying the corn before it can be stored or moved into market channels. Even corn that dries in the field to below 20 percent is likely to receive some drying since the market is based on 15-1/2 percent corn and a moisture content of 13 to 14 percent is desirable for long term storage. The installation of grain drying facilities by the producer has added another rather high management operation to his production system. Many producers of corn have progressed through a series of grain drying equipment as corn acreage, yields, and harvest rates have increased. Although not all will have used every system, the systems in use include:

1. In-bin or layer drying
2. Batch-in-bin drying
3. Batch-in-bin with grain stirring
4. Portable or semiportable batch dryer
5. Continuous flow dryer
6. Batch or continuous flow drying combined with dryeration

In general, the capacity in terms of bushels dried per unit time increases in the order as listed above. The temperature of the air used for drying increases in the same order. Management of the dryer in relation to good quality grain becomes more critical as the drying air temperature is increased.

Improper management, perhaps resulting from a desire to increase capacity or because of a labor shortage, has resulted in a loss of corn quality during the drying operation or in subsequent handling of the grain in some instances.

Techniques for grain conditioning continue to be investigated. One rather new development already in limited use is a method of low temperature grain conditioning and storage. The allowable storage or drying time can be greatly extended by maintaining grain at a low temperature. Low temperature drying and storage appears to have the potential for producing a high quality product.

Corn production, especially the harvesting and conditioning, is in the transition from ear corn and natural air drying to shelled corn and artificial conditioning. As a result, corn now has somewhat different characteristics as compared to corn 20 years ago.

RECENT DEVELOPMENTS IN CORN BREEDING
WITH RESPECT TO CORN QUALITY

D. E. Alexander

In late 1963, Bates, Mertz, and Nelson of Purdue University found that the endosperm of opaque-2 corn contained 70 percent more lysine than ordinary corn endosperm. Furthermore, tryptophan was comparably increased. Endosperm proteins in ordinary maize are notoriously poor, hence the finding immediately promised that revolutionary changes in corn quality were in the making. Trials with rats, swine, and humans verified that the new corn had superior feeding qualities.

The opaque-2 discovery should not be confused with earlier work at Illinois that succeeded in increasing the amount of protein in corn. The high-protein corns were notoriously low in quality, and they never achieved economic significance.

The Breeding of Opaque-2 Hybrids

Even though laboratory analyses and feeding trials established that opaque-2 corn was superior to ordinary corn in its protein quality, many questions remained unanswered, even as late as autumn, 1966. Could satisfactory opaque-2 hybrids be bred? Would the protein quality remain high if the yield was high? Would protein quality be excellent if protein quantity (percent) was increased?

As a consequence, the University of Illinois breeders (during the summer of 1964) made crosses between the genetic stocks and inbreds that are parents of good hybrids. Two generations per year were grown in an effort to shorten the time before hybrids could be tested. In 1966, 17 primitive opaque-2 single-cross hybrids and their normal counterparts were tested in field trials. Breeding continued in order to produce better versions of the same hybrids, as well as new ones. More comprehensive tests were conducted at three locations in Illinois in 1967. A summary of performance at Urbana is shown in Table 1.

From these trials we have concluded that opaque-2 hybrids:

1. Approach normal counterpart hybrids in yield. The average of opaque-2 hybrids was 92 percent that of normals in 1967 at Urbana.
2. Have a higher moisture content in the grain at harvest than normals.
3. Produce grain that is softer and is more likely to be damaged by machinery at harvest than are normals.
4. Do not germinate as well in cold soil as do normals.
5. May be more susceptible to ear rots than are normals.

The earlier questions concerning yield and protein quality were answered by the 1966-1967 trials: Amino acid analyses showed that yield was independent of quality, i.e., the highest yielding hybrid had high-quality protein. Nelson of Purdue had reported earlier that 15-percent protein corn carrying the opaque-2 gene was of similar quality to opaque-2 corn of lower (10 percent) protein content.

Jensen of Illinois, in experiments with finishing swine, showed that:

1. Soybean meal level could be reduced by 50 percent in finishing swine rations if opaque-2 corn was substituted for ordinary corn.
2. The performance of finishing swine fed opaque-2 corn plus crystalline lysine was equal to that of swine fed regular corn-soybean meal rations, even though the latter carried 12 percent and the former less than 10 percent protein. (Mineral and vitamin supplementation was identical in both rations.)

These results are particularly important, for if finishing swine (and presumably humans) can thrive on 10-percent protein diets (if lysine and tryptophan are not limiting), the advisability of breeding corns of 12- to 16-percent protein is much less appealing. Since opaque-2 corn contains 0.35- to 0.40-percent lysine and since the finishing-pig requirement for lysine is about 0.5 percent, the critical question then seems to be whether the level of lysine can be increased to that value by breeding. This question has yet to be resolved, but it is a prime feature of Illinois research.

The Future of Modified-Protein Corn

The first flush of research on opaque-2 corn has produced much valuable information. Breeders know that corn proteins need not be inferior to legume proteins. It seems inevitable that analytical techniques will soon be developed that will stimulate the development of hybrids equal in performance to the best normal hybrids. Even though the opaque-2 gene acts as an optical marker for high-lysine and tryptophan content, too little is known about variation existing within it. In our breeding work, we find near-normal segregates in material carrying the opaque-2 gene. Are they high, or even higher, in lysine? How will they perform in field trials?

A second genetic approach to the breeding of these revolutionary hybrids is through the use of another gene called floury-2, also discovered by the same team that made the opaque discovery. Floury-2 corn is quite similar to opaque-2 corn in appearance and protein quality. However, it may have some advantages. It appears to be slightly harder and denser than opaque-2. Primitive floury-2 hybrids and their normal counterparts will be tested at Urbana in 1968.

Still another approach remains open. Stocks carrying both opaque-2 and floury-2 are quite similar in appearance to regular dent corn, yet are high in quality. An evaluation of this corn in small-animal feeding trials will doubtless take place in late 1968. Preliminary breeding work is already underway.

Summary and Conclusions

1. The quality of corn endosperm proteins can be vastly and favorably modified by several genetic means.
2. Although not equal in yield to normal counterpart hybrids, opaque-2 hybrids do approach them. Opaque-2 hybrids were 8 percent lower in yield than normals in 1967 trials.
3. Opaque-2 hybrids tend to be higher in grain moisture, are softer, and may be more susceptible to ear rots than normal hybrids. Further breeding work is expected to improve these defects.
4. Feeding trials with swine have demonstrated that half as much soybean meal is required in finishing rations if opaque-2 corn is substituted for normal corn.
5. Experimental rations containing 0.5-percent lysine at a 10-percent protein level produced gains and feed-conversion ratios in finishing swine equal to those produced by a regular ration containing 12-percent protein. The wisdom of breeding corn for higher protein content can be questioned.
6. Several genetic alternatives are available to breeders in the building of high-quality protein corns.
7. It is reasonably probable that satisfactory hybrids containing 0.5-percent lysine and adequate tryptophan will soon be bred.

Table 1. Performance of Opaque-2 Hybrids and
Normal Counterparts, 1966-1967

	Yield (bu./a.)	Moisture in grain (percent)	Erect plants (percent)
Urbana, 1966			
All opaque-2 hybrids	105	26	97
Normal counterparts	124	24	92
R801 x R802 (opaque)	115	25	96
R801 x R802 (normal)	119	21	98
Urbana, 1967			
All opaque-2 hybrids	87	25	74
Normal counterparts	94	22	67
R801 x O7N (opaque)	98	24	77
R801 x O7N (normal)	98	22	93
(R801 x R802) O7N (opaque)	106	30	94
(R801 x R802) O7N (normal)	111	21	98

HERBICIDES FOR CORN-USE AND CONSUMER PROTECTION

Ellery L. Knake

The use of soil-applied preemergence herbicides has risen rapidly from 5 percent of the Illinois acreage treated in 1960 to over 50 percent treated in 1968. In addition, approximately 40 percent of the Illinois corn acreage is sprayed post-emergence with 2,4-D.

The use of 2,4-D began in the 1940's and provided effective, economical control of broadleaved weeds in corn.

During the 1950's several factors contributed to an intensified problem with annual grass weeds in corn. (1) A recently introduced annual grass, giant foxtail, spread rapidly. (2) Farmers switched from check planting corn to drilling and hill-dropping thus making control of weeds in the row more difficult. (3) Control of broadleaved weeds with 2,4-D allowed annual grass weeds more freedom to develop.

Fortunately preemergence herbicides were introduced to provide better control of particularly the annual grass weeds. Competition studies have indicated the extent of yield losses due to both annual grass and broadleaved weeds and indicate the economic advantage of herbicide use.

For a herbicide to be cleared, the manufacturer must submit data to the USDA to show that the chemical is effective for the intended purpose and that it will be useful. They must also submit data indicating that where the herbicide is used, food products will not contain residues or breakdown products of the chemical in sufficient quantity to be harmful to consumers.

Atrazine is one of the major preemergence herbicides used for corn. Corn has good tolerance to atrazine since the corn plant has the ability to detoxify the chemical. Atrazine may be applied prior to planting, at planting time or within 3 weeks after planting. An increasing amount of atrazine is being broadcast rather than just band applied over the row.

Ramrod is a recent introduction primarily for control of annual grass weeds. Most of the Randox formerly used is being replaced by Ramrod. This herbicide performs best on the darker soils and is usually band applied in granular form.

Several other herbicides and herbicide combinations are available for preemergence use such as 2,4-D ester, Knoxweed, Randox-T and Sutan. Herbicides vary considerably in such characteristics as solubility and persistence in the soil. Some are leached more rapidly than others. Some are decomposed more rapidly than others.

Many things can happen to soil-applied herbicides. They may be broken down by photodecomposition from sunlight on the soil surface and some can be lost from the soil by volatilization. In the soil, herbicides may be adsorbed onto clay particles or onto the organic matter complex. This can affect the availability to plants. Microorganisms in the soil are important in the decomposition of many herbicides. Certain chemical processes in the soil are also responsible for herbicide breakdown.

Usually only a few pounds of herbicide are needed per acre. But it is important to apply this "tremendous trifle" accurately and uniformly to avoid problems. Farmers are generally careful about applying recommended amounts at the proper time to the proper crop. Excessive amounts are not usually applied because of the increased cost and the possibility of damage to the present or subsequent crop.

Herbicides vary in their toxicity but the acute oral toxicity of most is not considered very high. Some, such as Radox and Ramrod are irritating to skin and growers need to use appropriate precautions when handling them.

Herbicides have a relatively good record as far as safety to consumers is concerned. Although continued vigilance and precautions are advisable, processors of corn products probably have little reason to be greatly concerned about any problems with most of the currently used herbicides.

HERBICIDE AND PESTICIDE RESIDUES IN CEREAL GRAINS

H. B. Sinclair

Insecticides fall broadly into three general types with some common insecticides as shown below:

<u>Organo chlorine</u>	<u>Organo phosphate</u>	<u>Carbamate</u>
Aldrin	Diazinon	Carbaryl
DDT	Malathion	Zectran (R)
Heptachlor	Methyl parathion	
Lindane	Phorate	

In Figure 1 is shown the chemical structure of aldrin, heptachlor, and DDT, three widely used organo chlorine insecticides. In soil and plant tissue the olefinic bond of aldrin and heptachlor is epoxidized to give dieldrin and heptachlor epoxide; as a result the insecticides are usually referred to as aldrin-dieldrin and heptachlor-heptachlor epoxide complexes.

Organo phosphate, as well as carbamate, insecticides contain a characteristic structural unit, shown in Figure 2. In general, the R_1 and R_2 groups in the organo phosphate are the same. When X is oxygen, the insecticide exhibits direct action and when X is sulfur, a hydrolytic product imparts the toxicity. Organo phosphate insecticides usually act as cholinesterase inhibitors.

Both carbaryl and zectran, carbamate insecticides, appear from present information to operate as shunts for biochemical oxidative processes.

Organo chlorine insecticides are insoluble in water and soluble in fat. They are stored in fatty tissue and are metabolized and excreted slowly (DDT's biological half-life is about 1 year). This aspect of biological stability and fat solubility has created a serious problem of progressive concentration along a food chain (ecological magnification) to a point where levels of the chloro-insecticide burden have caused severe damage to the reproductive capacity in some wild life.

Figure 3 shows a toxicity/persistency rating of some common insecticides. Insecticides of the organo phosphate and carbamate types are generally susceptible to hydrolysis. As a result, they are detoxified and excreted as derivatives in the urine. This prevents ecological magnification and fat storage.

Many factors influence the persistence of insecticides in soil, such as temperature, moisture, agricultural practices, soil type, and volatility. The residue of aldrin and its epoxide--dieldrin in soil is shown in Figure 4. Decker, Bruce, and Bigger concluded that "under Corn Belt conditions in Illinois the probability that annual applications of aldrin over a period of 10 years will result in accumulations in excess of the annual application rate is remote."

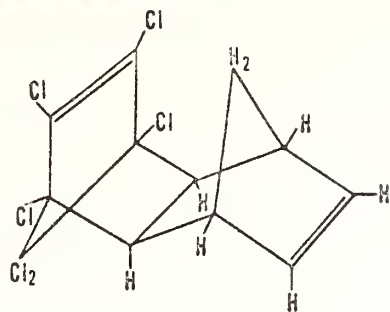
As higher levels of insecticides are applied to soil, higher levels are translocated to the seed residue, as shown in Figure 5.

A relationship between the seed residue and seed fat is shown in Figure 6 (application rate, 1 p.p.m.).

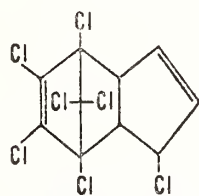
These results suggest that the translocation pathway and the fat synthesis mechanism are closely related for organo chlorine insecticides.

Figure 7 shows the latest reported residues in corn products. Using the Food and Agriculture Organization (FAO) acceptable daily intake values, one would need to consume 188 pounds of grain, 19.7 pounds crude oil, or 35 pounds refined oil each day to exceed the DDT recommendation.

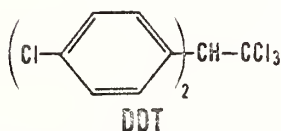
Organo Chlorine



Aldrin



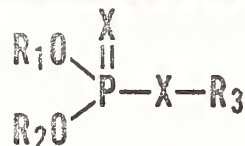
Heptachlor



DDT

Fig. 1 Chemical structure of insecticides

Organo Phosphate



X = S, O

Carbamate



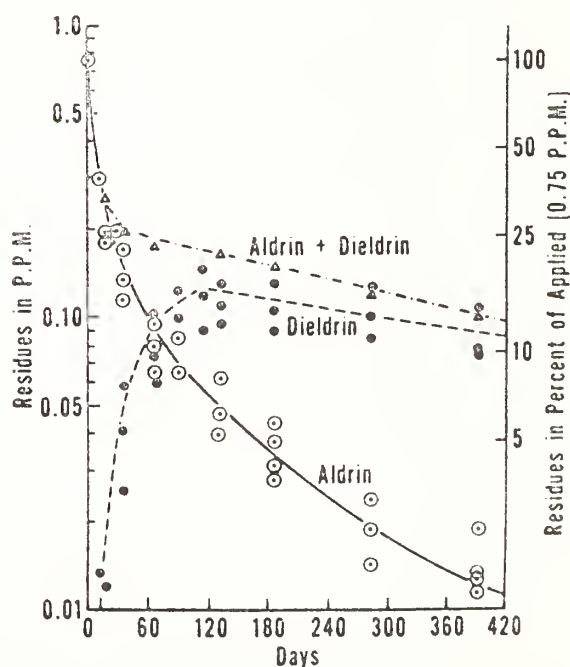
Fig. 2 Chemical structure of insecticides

	Toxicity	Persistency
<u>Organo chlorine</u>		
Aldrin	2	1
Heptachlor	2	1
<u>Organo phosphate</u>		
Malathion	5	6
Diazinon	3	3
<u>Carbamate</u>		
Carbaryl	4	3
Zectran ^(R)	2	3

1 = high toxicity and persistence

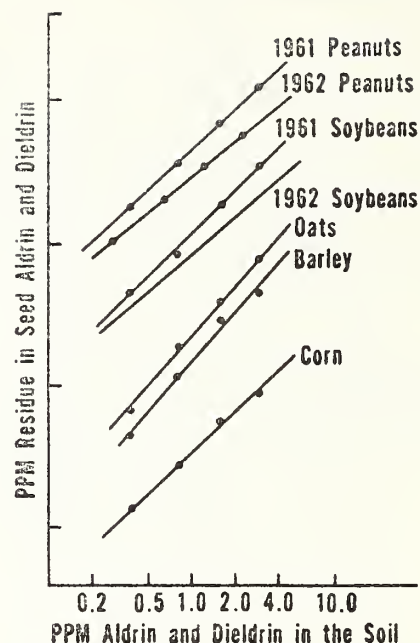
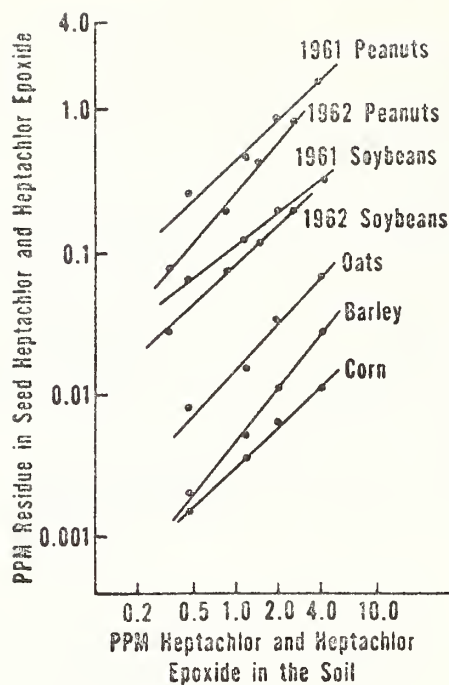
6 = low toxicity and persistence

Fig. 3 Toxicity/persistency rating of pesticides



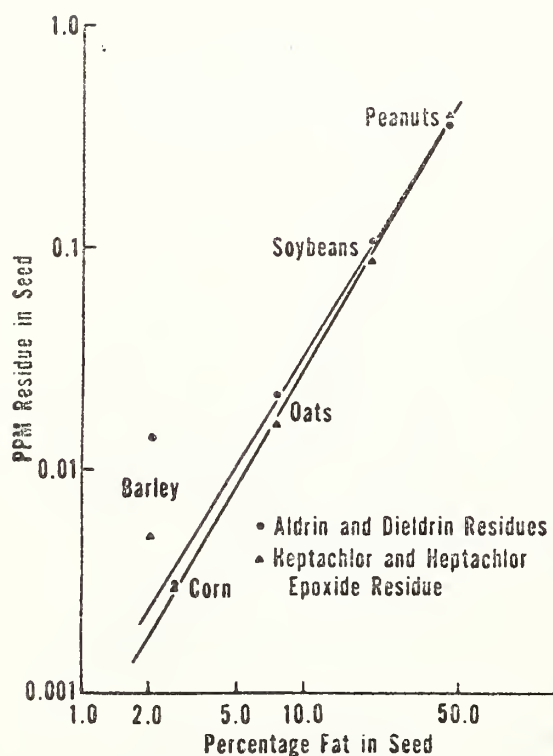
Decker, Bruce, Bigger (1965)

Fig. 4 Pesticide residues in soil



Bruce, Decker, Wilson (1966)

Fig. 5 Residue in crop



Bruce, Decker, Wilson (1966)

Fig. 6 Relationship of residue to oil content

	Percent of Samples Containing Specific Pesticides and Average Level [PPM] of Each Pesticide		
	Grain	Crude Oil	Refined Oil
DDT	5.7 (0.007)	14.8 (0.067)	12.5 (0.038)
DDE	1.2 (0.003)	11.1 (0.060)	12.5 (0.002)
Dieldrin	2.9 (T)	11.1 (0.016)	—
Lindane	4.4 (0.001)	11.1 (0.013)	—
Toxaphene	2.6 (T)	—	—
Endrin	—	—	—
Chlordane	0.1 (T)	—	—
	—	3.7 (0.080)	—
Total Number of Samples	819	27	8
Percent w/Residues	13.4	25.9	25.0

Duggan (1966)

Fig. 7 Pesticide residues in corn products
(T = <0.001 PPM; — = Not detected)

PROBLEMS AND NEEDS OF THE CORN WET MILLING INDUSTRY
(Open Discussion)

Mr. W. B. DeWitt: On behalf of the Corn Refiners Association and the Technical Advisory Committee, we would like to extend our thanks to you, Dr. Dimler, to Cliff Witham, and to all the speakers for the excellent program. Our Committee feels this is one of the best meetings of the year that they go to. Judging by the comments that I heard last night and this morning, this is particularly true this year. As you pointed out, this morning's session was new and different. I think George Inglett is to be congratulated on his "program fillers." Periodically, we might consider similar type reviews to catch us up on what is going on.

The agenda is open-ended from here on out. While our company research directors will express themselves very shortly, I would like to take a minute to review the ten suggested research areas for the industry that Mr. Liebenow presented in March of 1967 to the Grain and Forage Crops Research Advisory Committee. At that time, these were considered the needs of the industry, and I do not see that over the past 15 or 18 months the situation has changed much. These are as follows:

1. Study of phenomena of starch gels. This would include determination of the basic reaction in the swelling and gelatinization of starch granules as well as the physical and chemical factors causing variations in swelling and gelatinization.
2. Study of the mechanism and kinetics in the absorption of various types of starch and modified starch molecules by cellulose fibers and surfaces in internally sized systems.
3. Adhesion. Determine the adhesion of starch paste prepared by different methods and treatments, and physical and chemical structures of pastes differing in adhesive characteristics.
4. Research to produce food-grade protein by microbiological systems which use carbohydrates both as a nutrient and as a carbon source.
5. The development of "in-line" methods for the monitoring of dextrose equivalent, moisture, and protein.
6. Study of the technical aspects of total water management for the entire wet-milling industry with a view to decreasing demand, improving effluent quality, and developing technically sound procedures for utilization of recovered solids.
7. Existing knowledge of the significance of carbohydrates in human diets should be reassessed in modern terms as a guide for fresh research to put carbohydrates in their proper perspective.
8. Study complexes of inorganic ions with carbohydrates to increase utilization of starch in the metallurgical industries.
9. Trace the origin of undesirable cereal flavors in dextrins and starches, especially in pregelatinized types of starch, and develop methods to eliminate them.

10. Continue support for genetic studies to develop new varieties of high-amylose corn, high-lysine corn, and work to raise the antioxidant and xanthophyll levels in corn.

We are well aware of the fact that ARS has done and is doing quite a bit of work in some of these areas here at the Laboratory and through grants at colleges and universities and PL 480 grants. As you pointed out yesterday, with the current emphasis on dollar value of research and the shift in our research program, it behooves all of us to communicate closely our ideas and needs to you and for you to communicate what you are doing to us.

At this point, the meeting will open for discussion. The man to lead it off is Dr. E. L. Powell, who is chairman of our Technical Advisory Committee.

Dr. E. L. Powell: I see no reason to go over the list that Bill has read but I would suggest that our TAC group, which will be meeting shortly, may want to reword those, and perhaps rearrange them in some order of priority. I do not think it is fair to lay out ten projects and say that USDA should solve all of them for us immediately. I think it would be better for us to decide which ones are more important to tackle first, and then present a priority list. Item (1) may have covered this, but I want to comment on it myself. One of our most exasperating problems for 30 years has been the total broad problem of the rheology of starch pastes and gels. We have tried to get people to work on this material "as is", while the classical rheologists do not want to work on it "as is." They only want to relate it to molecular weight of the polymer; they always want to fit it into the classical equations; where does it fit? As a consequence, much of this work, while interesting theoretically, has not been of direct help to our industry. What we need, I think, is a multidirectional approach to rheology of these materials. In other words, study starch pastes in 5 percent, 10 percent stocks; study the changes that occur in cooking, and mechanical shearing; study the changes with age. All of these things are what we are faced with every day and what our customers face. The material in a swollen starch granule in a water system is rarely in equilibrium; and this makes the one-point determination useless, that is, one point in time. We have not been able to get this story across to the theoretical rheologists. I thought the last time we met here that the group at Peoria was starting to make some progress in this direction; perhaps it is still going on. We did not hear about it anyway, but I certainly hope we do; that is, more work along the lines of rheology.

There are two areas that I know we are going to be discussing this afternoon and tomorrow, where the USDA might be in a position to do our industry a very great service. One would be a microbiological survey of our industry; not just for the grain, but also in food processing, if we could get all of the companies to agree to let people in to get samples and to furnish samples. When I say microbiological, it would not be just the aflatoxin problem, but would include other toxins which are produced by microorganisms about which we might be concerned. We always have problems of Salmonellae, E. coli, etc., and thermophiles in various products. It might be that a broad industrywide survey could do us a lot of good. Our Board of Trustees have expressed interest in this. Another type of survey for which we might work up a program with someone

in USDA would be one such as we heard alluded to this morning of pesticides, not only in the grain but also how they carry through our processes. Where do they concentrate? Where disappear?

Dr. R. J. Dimler: Might I make one comment, Gene; in your deliberations on this microbiological survey, one service you can do me will be to try to pinpoint why we (USDA) should do it instead of the industry doing it. After all, you have in your industry a fair amount of microbiological expertise. It may be in a limited number of companies, but you do have it; so that there will need to be some reason why the taxpayer, through the Department, should do this instead of the industry itself.

Mr. C. H. Hullinger: One of two areas of specific projects which would be of interest to us and perhaps to several of the other industries as well, is to develop an instrument which would serve as a recording viscometer at temperatures going above 212° F. As you know, in augur-jet cooking we are going up to all kinds of temperatures. All that we can do is to measure the temperatures of the finished products after they have flashed off and cooled. No one knows what happens to the viscosity during this time and temperature exposure. In all the retorting and canning industry, no one really knows what is happening in the can. During retorting, of course, this is a real factor in determining the time needed for sterilization. Very frankly, I do not think anyone can tell us the viscosity of a starch paste above the boiling point. It requires a different type of sensing element, but it should not be too difficult to build for someone who is mechanically inclined and who would tie into it. This is the general problem.

Another thing that we should consider, as the talks we heard this morning pointed out, is the changes that have taken place in corn over the past few years in terms of genetic variety, mechanical damage, drying and processing of different types. When you stop to think that our steeping work goes back perhaps a generation and may have been optimum at that time, it would be very surprising if it were optimum steeping today. One of our difficulties in getting a handle on this is that we do not have, as yet, an in-process test that would predict whether a particular tank of corn was steeped the right amount of time. I have been looking in the laboratory with limited success, or perhaps none, to find a test that will say that this starch-protein slurry can, at this point, be easily separated by mechanical means in our centrifuges and in other steps on down the line.

It is not too difficult to take out the germ; this is no problem. To do this you take the fiber out by various screens. But then you have the starch-protein stream; and you have some isolated starch granules which should come out fairly easily, and some isolated protein fragments which should come out easily. But there is bound to be some little fraction in there or aggregate where you have the matrix still in existence. This particular "middle cut" is the one which runs around and around and ends up in one stream or another and gets you into trouble. If we could identify quantitatively the troublesome portion of this middle stream and say that it was not steeped long enough, or it was steeped too long, or was not ground fine enough; I think these are two areas which would be of concern to all of us.

Mr. DeWitt: Jim, this sort of ties into something you were talking about one time in Chicago on the wet-milling process. Would you like to expound on that a little?

Dr. J. A. Bralley: I do not know that I can expound on it very much, but I think that we have all seen this or something very similar for years. I have not made a concentrated study of the steeping process myself, but there might be better ways to do it, whether you use sulfur dioxide or something else.

In another area, I would like to say that of the specific talks we heard yesterday, our own company would be most interested in seeing work continued on the amylose starch film, especially along the line of studying food-acceptable plasticizers, and for further modifying the high-amylose starch by derivatization in order to get better physical properties, tensile strength, etc., at higher humidities and lower temperatures.

We are also quite interested in the immobilization of enzymes; there is industry-wide interest in this problem. The work on the amino acid analytical technique is very interesting to me. As you know, we still need a better method for measuring protein content rapidly. This is a very difficult problem and I hope you complete the work on it. I believe the mycotoxin survey on corn, which I understand is extended to this year, too, is a very important study. This morning, I was especially interested in Dr. Alexander's talk on high-lysine corn. I hope that they will develop types that are hard enough to handle without breaking the grains down to powder. That is all I have to say.

Dr. C. G. Caldwell: I think that we have a lot more to learn about the structure of grain. We still need to know a lot more about what happens in starch films, both what the situation is and what kind of changes take place. These things may not be basic studies, but they are definitely related. For instance, starch in adhesives, and starch absorbed on wood fibers, and so on. We still need a lot of what I call basic studies in the behavior of these materials. I think most of these, in spite of the Laboratory's basic charter which is to increase corn usage, are projects which could be justified on the basis of economic analysis or market research.

Dr. John Garber: I think one of the problems here is that if each of us gives his idea of the problem it is going to be rather confusing. As Gene says, it would be better if we put our heads together and come up with a list of things which we can sell to management. The basic part is what is hard to justify; but that is the part we need. To help you do this, and this may be the problem, it resolves to, "What can we do to give you the ammunition you need to sell basic research?" Maybe we can help fill in some of these knowledge gaps.

Also, we have a water problem. Just how can we resolve this? It's on your list, Bill, but what can we do about it? We might combine a program on how to clean up effluents with one on how to make protein from carbohydrates.

Dr. Kenneth W. Kirby: The only comment that I would make is that one of the things we are faced with, whether we care about it or not, is the one of higher protein, higher oil, and higher moisture corn. It would seem that it is necessary to know more about extraction and separation; that's what we ought to know more about.

Dr. Ronald E. Pyle: One question I've been asking about, perhaps similar to one previously raised, although I might frame mine differently, "What influence does corn grading have on yield of starch? What grade factors affect us? Insect damage? Kernel damage? How do these associate with yield?"

Dr. B. L. Scallet: I think we've pretty well covered everything, but I would like to make a few comments. It has been said that there is good research and bad research, but there is not really much difference between basic and applied research. With basic research, one just has yet to develop applied uses, assuming it isn't bad basic research. I think special care should be taken in every analytical technique starting with the sample collected. Sample collecting procedures can be devised that will give an overall picture of what we are trying to see; and also sample preparation procedures devised that will give an overall picture of what we are studying.

We could be working on a number of things that are common to the industry: analyses for herbicides, pesticides, microbiology.

Mr. W. DeWitt: The area of rapid and accurate analytical methods for determining hardest components is of interest to our industry. I don't think we can emphasize this too much. This is a program that our Board of Trustees are much in favor of. A great deal of the analytical work has been done through a subcommittee of our Technical Advisory Committee, known as the Analytical Subcommittee. It seems to me very possible that this Laboratory could involve itself in general analyses of this type; the main aim being to acquire more information rapidly and at low cost.

We have pretty well polled the delegation, now. Do any of you have questions for any of our members? If not, that should about tie it up.

Bob, I think most of us have expressed our appreciation individually but I would like to add the Committee's thanks to you. I think it was an excellent job over this entire day and a half. There were some excellent papers, well presented, and very informative.

Dr. R. J. Dimler: Thank you. I appreciate these comments. In closing the meeting then, I would like to again thank the Technical Advisory Committee for meeting with us. We will look forward to further feed-back from you relative to needs for research, particularly where we as an organization might help to fill those needs. We will look forward to having you back again and wish you good deliberations in the remaining time you are to be in town.

The meeting is adjourned!

Attendance List

CORN INDUSTRIES RESEARCH FOUNDATION, Washington, D.C.

William G. DeWitt

CORN REFINERS ASSOCIATION, INC., Washington, D.C.

Robert C. Liebenow

AMERICAN MAIZE-PRODUCTS COMPANY, Roby, Indiana

E. L. Powell
C. H. Hullinger

ANHEUSER-BUSCH, INC., St. Louis, Missouri

B. L. Scallet

CLINTON CORN PROCESSING COMPANY, Clinton, Iowa

E. K. Crosby
N. E. Lloyd

CORN PRODUCTS COMPANY, MOFFETT TECHNICAL CENTER, Argo, Illinois

John D. Garber
E. F. Paschall
R. J. Smith

HUBINGER COMPANY, Keokuk, Iowa

Waldean G. Rapp
J. M. Seitz

PENICK AND FORD LIMITED, Cedar Rapids, Iowa

Kenneth W. Kirby

A. E. STALEY COMPANY, Decatur, Illinois

J. A. Bralley
E. E. Fisher

NATIONAL STARCH AND CHEMICAL CORPORATION, Plainfield, N.J.

C. G. Caldwell
Hans Stockman
O. B. Wurzburg

UNION STARCH AND REFINING CO., INC., Granite City, Illinois

Ronald E. Pyle
Ron Weiss

UNIVERSITY OF ILLINOIS, Urbana, Illinois

G. C. Shove
D. E. Alexander
E. L. Knake

NORTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION, Peoria, Illinois

R. J. Dimler
W. C. Witham
H. M. Teeter
D. L. Miller
J. E. Hubbard
K. R. Majors

Cereal Products Laboratory

C. E. Rist
C. R. Russell
W. M. Doane
A. M. Mark
R. A. Buchanan
G. G. Maher
B. T. Hofreiter
F. H. Otey
C. L. Mehlretter
J. C. Rankin

Cereal Properties Laboratory

G. E. Inglett	C. W. Blessin
J. Lehrfeld	Y. V. Wu
J. F. Cavins	H. C. Nielsen
M. J. Wolf	J. W. Paulis
H. B. Sinclair	D. Christianson
J. S. Wall	C. James
J. E. Hodge	U. Khoo
T. D. Simpson	H. W. Gardner
	G. W. Grams

Engineering and Development Laboratory

E. L. Griffin	C. Vojnovich
V. F. Pfeifer	A. J. Peplinski
R. A. Anderson	H. F. Conway
G. N. Bookwalter	O. L. Brekke
A. C. Stringfellow	

Fermentation Laboratory

C. W. Hesseltine
A. Ciegler
G. W. Strandberg
C. P. Kurtzman
Marilyn Bachler
H. R. Burmeister